

**Dieses Dokument ist eine Zweitveröffentlichung (Verlagsversion) /
This is a self-archiving document (published version):**

Oliver Eberhardt, Thomas Wallmersperger

**Molecular mechanics methods for individual carbon nanotubes and
nanotube assemblies**

Erstveröffentlichung in / First published in:

SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring.
San Diego, 2015. Bellingham: SPIE, Vol. 9432 [Zugriff am: 02.05.2019].

DOI: <https://doi.org/10.1117/12.2084209>

Diese Version ist verfügbar / This version is available on:

<https://nbn-resolving.org/urn:nbn:de:bsz:14-qucosa2-350326>

„Dieser Beitrag ist mit Zustimmung des Rechteinhabers aufgrund einer (DFGgeförderten) Allianz- bzw. Nationallizenz frei zugänglich.“

This publication is openly accessible with the permission of the copyright owner. The permission is granted within a nationwide license, supported by the German Research Foundation (abbr. in German DFG).

www.nationallizenzen.de/

PROCEEDINGS OF SPIE

[SPIDigitalLibrary.org/conference-proceedings-of-spie](https://www.spiedigitallibrary.org/conference-proceedings-of-spie)

Molecular mechanics methods for individual carbon nanotubes and nanotube assemblies

Oliver Eberhardt, Thomas Wallmersperger

Oliver Eberhardt, Thomas Wallmersperger, "Molecular mechanics methods for individual carbon nanotubes and nanotube assemblies," Proc. SPIE 9432, Behavior and Mechanics of Multifunctional Materials and Composites 2015, 94320G (1 April 2015); doi: 10.1117/12.2084209

SPIE.

Event: SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring, 2015, San Diego, California, United States

Molecular mechanics methods for individual carbon nanotubes and nanotube assemblies

Oliver Eberhardt^a and Thomas Wallmersperger^a

^aInstitut für Festkörpermechanik, George-Bähr-Straße 3c, Technische Universität Dresden, Germany

ABSTRACT

Since many years, carbon nanotubes (CNTs) have been considered for a wide range of applications due to their outstanding mechanical properties. CNTs are tubular structures, showing a graphene like hexagonal lattice. Our interest in the calculation of the mechanical properties is motivated by several applications which demand the knowledge of the material behavior. One application in which the knowledge of the material behavior is vital is the CNT based fiber. Due to the excellent stiffness and strength of the individual CNTs, these fibers are expected to be a promising successor for state of the art carbon fibers. However, the mechanical properties of the fibers fall back behind the properties of individual CNTs. It is assumed that this gap in the properties is a result of the van-der-Waals interactions of the individual CNTs within the fiber. In order to understand the mechanical behavior of the fibers we apply a molecular mechanics approach.

The mechanical properties of the individual CNTs are investigated by using a modified structural molecular mechanics approach. This is done by calculating the properties of a truss-beam element framework representing the CNT with the help of a chemical force field.

Furthermore, we also investigate the interactions of CNTs arranged in basic CNT assemblies, mimicking the ones in a simple CNT fiber. We consider the van-der-Waals interactions in the structure and calculate the potential surface of the CNT assemblies.

Keywords: carbon nanotube, molecular mechanics, single wall nanotube, mechanical properties, modeling, nano, CNT

1. INTRODUCTION

Carbon nanotubes are considered as a promising material for a multitude of different applications due to their outstanding mechanical, electrical and thermal properties. This results in the still ongoing interest for this material based on the discoveries made by Iijima¹ in 1991. Since then, carbon nanotubes have been the subject of numerous and manifold studies. This includes the investigation of their properties as well as the consideration of this fascinating material for versatile applications.

A carbon nanotube (CNT) can be imagined as a single hollow cylinder made out of a cut-out in a graphene layer which was rolled up. This imaginary process creates a seamless tubular structure which is known as single wall carbon nanotube (SWNT). Several nested SWNTs create a multi wall carbon nanotube (MWNT). Due to the affinity of the CNTs to graphene and fullerenes the CNTs also show the typical hexagonal structure which is characteristic for this kind of carbon material. At each corner of the hexagon one can find a sp^2 -hybridized carbon atom which is connected to its three neighbors via covalent bonds. For a more detailed description of the carbon nanotubes see section 3 of this paper. Regarding the mechanical properties, the carbon nanotubes show an excellent stiffness and strength. This makes them a promising candidate for applications e.g. in lightweight constructions.

As already mentioned, the current interest in carbon nanotube related research was triggered by the work of Iijima et al.¹ However, the current status of carbon nanotube history research states, that the credit for their discovery should be given to the soviet scientists Radushkevich and Lukyanovich.² During their work on carbon formation by thermal decomposition they found tubular carbon structures of approximately 50 nm diameter.

Further author information: (Send correspondence to O. Eberhardt)

E-mail: Oliver.Eberhardt@tu-dresden.de, Telephone: +49 (0)3 51 463-33 401

Nevertheless one of the major contributions of Iijima to carbon nanotube related research, besides the rediscovery of CNTs, was his attempt to fill carbon nanotubes with metals, which resulted in the formation and discovery of single wall carbon nanotubes.

A large variety of possible applications of CNTs has been proposed during the last years. In the following, only the applications related to the mechanical behavior of CNTs are mentioned. CNTs in large quantities have been used as an additive to several materials in order to improve the properties of the basic material. For instance the addition of a given mass percentage of CNTs into polymers creates a composite with improved electrical conductivity as well as improved mechanical stability.³ Another effect resulting from the addition of CNTs into polymers or also into the matrix of carbon reinforced plastics is the increased damping of the resulting structure which was already used for instance in tennis rackets.⁴ CNT bulk material can also be used to create bucky paper. Bucky paper can be described as a kind of felt made of CNTs. As macroscopic actuators made out of a vast number of nanoscopic carbon nanotubes, Baughman et al.⁵ proposed a bucky paper actuator which is basically made out of a bucky paper strip which is immersed in an electrolyte. After the application of an electric voltage the bucky paper bends depending on the polarity and on the absolute value of the voltage.

The above mentioned applications rely on the usage of a vast number of CNTs which are irregularly arranged. However, also applications based on a predefined spatial order of the nanotubes have been considered. One can refer to these structures as nanotube assemblies. An example for such a structure can be a carbon fiber which was spun out of CNTs, e.g. see Lu et al.⁶ The creation of these carbon fibers was done with the hope, that the excellent mechanical properties of the individual carbon nanotubes are transferred onto the carbon nanotube fiber. However, the mechanical properties of the fiber differ significantly from the properties of the individual carbon nanotube. It is assumed, that this is due to the interactions between the CNTs in the fiber. This raises the question, if this interaction behavior can be investigated in more detail using numerical simulations. The importance of the (numerical) calculation of the material parameters is even more emphasized by the circumstance that the experimental determination of these parameters is highly challenging due to the nanoscopic size.

CNT fibers have also been proposed to be used as torsional actuators, see for instance Foroughi et al.⁷ A comprehensive review on more nanocarbon based actuators is also given in Kosidlo et al.⁸ A more extensive review regarding the applications of carbon nanotubes in general was given by Schnorr and Swager⁹ and De Volder et al.⁴

Inspired by the multitude of different applications of carbon nanotubes, the present work deals with methods of calculating the mechanical behavior of individual CNTs as well as of CNT assemblies. The reason why these are two cornerstones for the understanding of structures made of CNTs is again best explained with the example of the carbon fiber spun from individual carbon nanotubes. The behavior of the fiber is governed (i) by the mechanical properties of the individual carbon nanotubes and (ii) by the interaction behavior between the nanotubes in the assembly.

The present paper is structured as follows. After this introduction, section 2 gives a brief literature review concerning the modeling of the mechanical behavior of individual CNTs as well as of CNT assemblies. Section 4.1 shortly presents the model applied in order to calculate the elastic constants of individual CNTs. The results obtained with this model are shown in section 4.2. The methods applied for the investigation of CNT assemblies are introduced in section 5.1, and the results for a pull-out test case are given in section 5.2. The present paper is closed with concluding remarks and a short outlook in section 6.

2. LITERATURE REVIEW

Since the need for material parameters was recognized early, also several approaches to cope with this demand have been developed. It is possible to distinguish (i) methods to analyze individual CNTs and (ii) methods capable of analyzing assemblies of CNTs.

The numerical methods which are currently used to investigate the mechanical properties of individual CNTs can be coarsely subdivided into three classes of approaches. These are

- atomistic ab-initio calculations based on the solution of the Schrödinger equation
- classical continuum mechanics models
- classical models applying discrete structure elements.

The first group, the ab-initio approaches, are based on the calculation of the electronic states of the atoms in the investigated structure. This requires the solution of the Schrödinger equation. However, the calculation of the solution without any simplification is only possible for very simple systems. Hence, several assumptions and simplifications were introduced leading to methods like the density functional theory (DFT) and tight-binding methods (TBM) for example. Still, these methods are limited to systems with a relatively small amount of atoms. Nevertheless, these methods have been applied in order to calculate the mechanical behavior of individual carbon nanotubes. The DFT was applied for instance by Sánchez-Portal et al.¹⁰ for the calculation of structural, elastic and vibrational properties of CNTs. Domínguez-Rodríguez et al.¹¹ also applied the DFT as well as a molecular structural mechanics approach in order to compare the results of the different methods. Their calculation aimed on the determination of elastic properties. An example for the application of the TBM for the calculation of elastic properties of nanostructures including CNTs was given by Hernández et al.¹²

The application of classical continuum mechanics in the context of applying it for the description of CNTs incorporates mainly the calculation of equivalent continuum structures. Such an equivalent continuum structure for a CNT can be for instance a hollow cylinder made out of a shell using a continuous material, like it was proposed by Odegard et al.¹³ While their model assumes a linear elastic, isotropic material, the work done by Chang¹⁴ applies an anisotropic shell model.

The third class of approaches mentioned here is the one which is applied in the present work in order to model the mechanical behavior of individual carbon nanotubes. The approaches assigned to this group apply classical mechanics, but also try to account for the discrete structure of the CNTs consisting of the carbon atoms and the covalent bonds. As a result of this, the model applies beam elements or torsional and longitudinal springs. The details of the beam based approach are given in section 4.1 of this work.

The idea of using beam elements as representation for the covalent bonds in CNTs was first proposed by Li and Chou.¹⁵ The definition of the parameters mandatory to describe the beam are calculated from chemical force field descriptions. Details on the method are given in section 4.1. Based on the work of Li and Chou, Tserpes and Papanikos¹⁶ extended the model which facilitated the applicability of the model in commercial finite element tools. The model have been then used to calculate elastic properties such as the Young's modulus, the shear modulus as well as the Poisson ratio. The deformation mechanisms and the deformation behavior of SWNTs have been studied in more detail by Eberhardt and Wallmersperger.¹⁷ The model applied for this investigation was the one proposed by Li and Chou with the already mentioned extensions given by Tserpes and Papanikos. Further extensions/modifications of the model have been also proposed for instance by Chen et al.¹⁸

Another possibility concerning discrete structure elements for the representation of CNTs is the usage of systems of longitudinal and torsional springs. Again aiming on the calculation of elastic properties this has been done for instance in the work of Meo and Rossi,¹⁹ or even by just applying translational spring elements, by Giannopoulos et al.²⁰

Furthermore, the present work also deals with the investigation of CNT assemblies, where an assembly is a structure consisting of several CNTs. The CNTs can interact with each other via van-der-Waals forces. In order to analyze the behavior of this kind of structures, methods which are different from the ones used to calculate the behavior of individual CNTs are applied. A possible approach is the investigation of a potential surface. The potential surface is calculated by taking all relevant van-der-Waals contributions into account. Afterwards the potential surface is analyzed, i.e. maxima and minima are calculated in order to find equilibrium states of the CNT assembly. As a representation of the individual van-der-Waals contributions the Lennard-Jones potential is used. More details can be found in the corresponding section 5.1. Regarding this field of CNT research, the interested reader is referred for instance to the work of Zhao et al.²¹ They investigated the cohesive energies between carbon nanotubes and graphene and other substrates by applying several methods. A state-of the art molecular dynamics simulation was used. In addition, the authors developed a continuous analytical solution to selected problems.

3. CARBON NANOTUBE TYPES AND GEOMETRY

As already mentioned in section 1, a carbon nanotube can be imagined as a cut-out from a layer of graphene which is afterwards rolled up into a seamless tube. Due to the similarity of CNTs compared to graphene, the governing structure within the tube is the hexagon. One can find the carbon atoms located at each corner of the hexagons, and since the atoms are sp^2 -hybridized they form three covalent bonds to their three neighboring atoms. The fourth valence electron forms a π -bond to the adjacent atoms.

Carbon nanotubes can be classified into different types. The first classification of carbon nanotubes involves the number of incorporated shells. It is possible to distinguish between single and multi wall carbon nanotubes. As the name suggests, the single wall carbon nanotube is made out of a single graphene layer. Hence, multi wall carbon nanotubes are basically several single wall carbon nanotubes stacked together. Furthermore, the single wall carbon nanotubes can be distinguished into three sub types. These types are called armchair, zig-zag and chiral type. The different types are constructed from different unit cells. A unit cell is the basic construction element of a CNT, a particular number of concatenated unit cells creates a CNT of the desired type and length. The nanotube type can be described with the help of the so called index pair (n, m) , where n and m are natural numbers with $n \geq m$. With the knowledge of this index pair and the knowledge of the lengths a_{C-C} of the covalent bonds in the CNT it is possible to calculate the geometry of the CNT unit cell. The index pairs $(n, 0)$, (n, n) and (n, m) depict zig-zag, armchair and chiral SWNTs, respectively. An example of a CNT unit cell of each type is given in figure 1. For more details on the exact computation of unit cells, the interested reader is referred to the publications by Dresselhaus et al.²² and Cox and Hill.²³ The latter approach was used in the present work for the calculation of the CNT geometry.

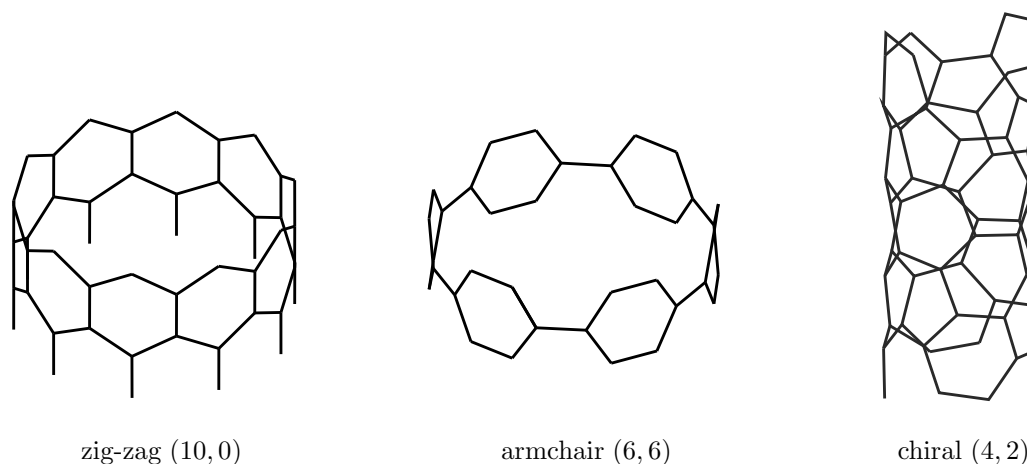


Figure 1. Schematic representation of a zig-zag, armchair and chiral unit cell

4. MECHANICAL PROPERTIES OF SWNTS

4.1 Modeling

This section briefly describes the model we applied in order to calculate elastic properties of SWNTs. In general, the modeling of CNTs can be divided into two parts: The first part describes how the geometry of the CNTs is taken into account. Concerning the nanotube geometry, the present work applies the exact polyhedral model developed by Cox and Hill.²³ The second part includes the representation of the covalent bonds in the carbon nanotube. This is done in the present work by using a molecular structural mechanics approach. In this kind of approach the covalent bonds are modeled by using truss-beam elements. The original approach was developed by Li and Chou¹⁵ but it has been modified and enhanced by the authors of the present paper in order to resolve some inconsistencies.

The application of beam elements requires the calculation of the geometrical parameters of the beam, as well as of the properties of the material the beam is made of. These properties are calculated using the chemical description of the CNTs which is based on the application of chemical force fields. To do this, it is necessary to identify at first possible bond deformations occurring in the CNTs. These deformations are (i) the bond stretching, (ii) bond torsion and (iii) bond angle bending, see figure 2. These deformations can be described mathematically by their corresponding chemical potentials stemming from a chemical force field description. In the present work, a chemical force field based on harmonic potentials is used. Figure 2 assigns the potentials to the deformations. The parameters k_r , k_θ and k_τ are called chemical force constants and the deformation

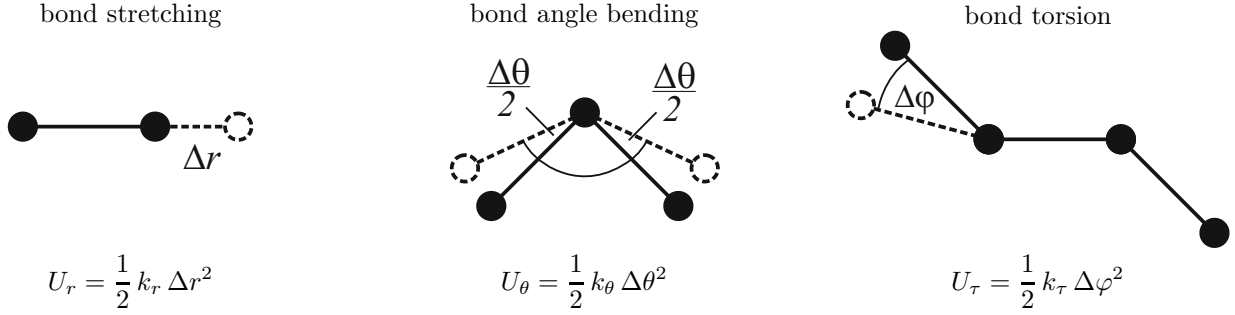


Figure 2. Bond deformations and their corresponding chemical potentials

variables are Δr for bond stretching, $\Delta\theta$ for the bond angle change and $\Delta\varphi$ for the torsion of the bond. The CNT structure is now described by using a truss-beam framework, we refer to this as mechanical representation of the CNT. A single beam in the framework is able to be deformed in three different manners: (i) beam stretching, (ii) beam bending and (iii) beam torsion, see figure 3. In this figure Δl is the stretching of the bond, $\Delta\alpha$ is the bending angle and $\Delta\beta$ is the torsion angle.

The approach to connect the chemical representation and the mechanical representation of the CNTs is to compare the total deformation works. The deformation work W_{chem}^{total} of a deformed CNT can be calculated with the chemical potentials by

$$W_{chem}^{total} = \sum_{i=1}^{N_r} \frac{1}{2} k_r \Delta r^2 + \sum_{i=1}^{N_\theta} \frac{1}{2} k_\theta \Delta \theta^2 + \sum_{i=1}^{N_\tau} \frac{1}{2} k_\tau \Delta \varphi^2. \quad (1)$$

The total work is the sum of the contributions due to bond stretching, bond angle change and bond torsion. N_r , N_θ , and N_τ are the total numbers of the corresponding bond deformations (number of occurring bond stretching, bond angle bending and bond torsion, as given in figure 2) occurring in the CNT structure. In the mechanical

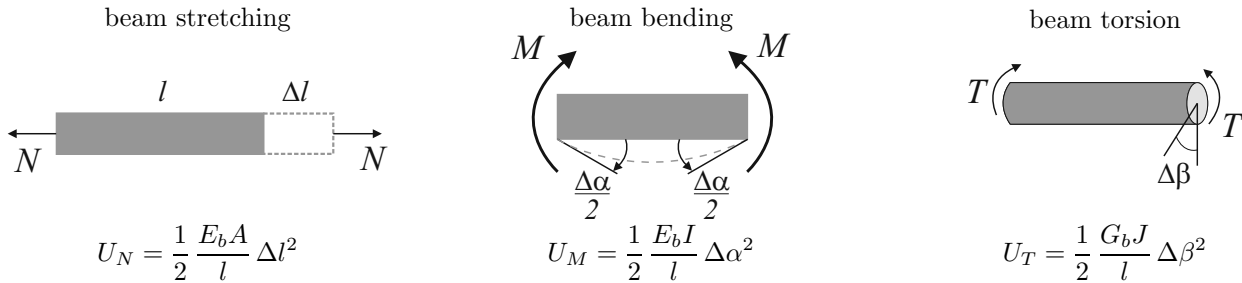


Figure 3. Beam deformations and their corresponding mechanical potentials

representation, the overall deformation work of the beam framework representing the CNT can be formulated as

$$W_{mech}^{total} = \sum_{i=1}^{N_e} \frac{1}{2} \frac{E_b A}{l} \Delta l^2 + \sum_{i=1}^{N_e} \frac{1}{2} \frac{E_b I}{l} \Delta \alpha^2 + \sum_{i=1}^{N_e} \frac{1}{2} \frac{G_b J}{l} \Delta \beta^2, \quad (2)$$

where N_e is the total number of beams in the beam framework. In this equation, E_b is the Young's modulus and G_b is the shear modulus of the beam material, l is the length of the beam which is equal to the length of a single bond. Furthermore, A , I and J are the cross sectional properties of the beam which are the cross sectional area, the moment of inertia with respect to bending and the moment of inertia with respect to torsion. Since equation (1) and equation (2) both describe the total deformation work of the CNT, they can be equalized

$$W_{chem}^{total} = W_{mech}^{total}. \quad (3)$$

Furthermore, one can notice, that in equation (1) as well as in equation (2) the total deformation work is decomposed into their different components. This enables the correlation of the bond stretching to the beam stretching, the bond angle change to the beam bending and the bond torsion to the beam torsion. The correlation of the contributions will then result in equations enabling the calculation of the beam parameters in dependence of the chemical force constants. Before performing the determination of the demanded parameters, some assumptions have to be made: With the assumption of a circular cross section with diameter d_b one can define the area and the moments of inertia as

$$A = \frac{\pi}{4} d_b^2; \quad I = \frac{\pi}{64} d_b^4; \quad J = \frac{\pi}{32} d_b^4. \quad (4)$$

Furthermore, in the present work only small deformations of the CNTs are considered due to the following reasons:

- The applied harmonic potentials are only a good approximation of the bond behavior for small bond deformations.
- For the calculation of the Young's modulus a linear elastic behavior is assumed.

After the incorporation of the above mentioned assumptions and definitions, the correlation of the related bond and beam deformation works results in the desired geometrical and material information mandatory to define the beam elements

$$E_b = \frac{k_r^2 l}{2\pi k_\theta}; \quad G_b = \frac{k_r l k_r^2}{2\pi k_\theta^2}; \quad d_b = 2\sqrt{2} \sqrt{\frac{k_\theta}{k_r}}. \quad (5)$$

These parameters were used to set up the beam framework representation of carbon nanotubes in an FE-tool. In the present work ABAQUS was used for the implementation of the model.

4.2 Numerical simulation and results

The goal of the present study was the determination of elastic properties of carbon nanotubes, in particular the Young's modulus and the Poisson ratio. In order to obtain these material parameters, a numerical simulation of a virtual tensile test was conducted. This was done by fixing the nanotubes at one end while pulling with a predefined force at the other end. Due to the nanotube geometry, the tensile force was distributed equally onto the last atoms of the CNTs in order to avoid the introduction of any bending moments. The Young's modulus can then be calculated from the applied force, the original nanotube length and the displacement of the nanotube end. A linear elastic behavior of the CNT according to Hooke's law is assumed. The assumption of this kind of material behavior seems reasonable, since only small deformations of the CNTs were considered. In addition, the knowledge of the cross sectional area of the CNT is mandatory in order to compute a Young's modulus. The definition of the elastic parameters on the nanoscale poses some challenges and needs to be briefly mentioned: Since a SWNT is a structure made of only one atomic layer, the question arises what the physical dimension of the "wall" in terms of a thickness is. This work applies the most commonly used assumption, in which the interlaminar spacing of graphite (0.34 nm) is used for the wall thickness of the CNTs. This is done to assure a simple comparability of the results given in the present paper with works done by other authors. However, the general discussion if the transfer of material properties - defined originally for a continuum - on the nanoscale is useful or not, is still ongoing.

Beside the Young's modulus also the Poisson ratio is calculated. An analogous drawback concerning the definition of this elastic material property has also to be faced. In the present work, the Poisson ratio of CNTs is defined as the negative ratio of the radial strain to the strain in transversal direction.

In the present work, the investigation of CNTs comprises armchair nanotubes ranging from index pair (2, 2) to (10, 10) as well as zig-zag nanotubes ranging from (3, 0) to (17, 0). The results for both elastic constants (Young's modulus and Poisson ratio) are given in the figures 4 and 5.

Figure 4 shows, that the Young's modulus for armchair as well as for zig-zag tubes, at least for larger diameters, is found at approximately 0.8 TPa. This result emphasizes the outstanding mechanical properties of the CNTs. The Poisson ratio for armchair CNTs is nearly constant $\nu = 0.275$. For zig-zag nanotubes, ν increases with the CNT diameter until the same value of the Poisson number $\nu \approx 0.275$.

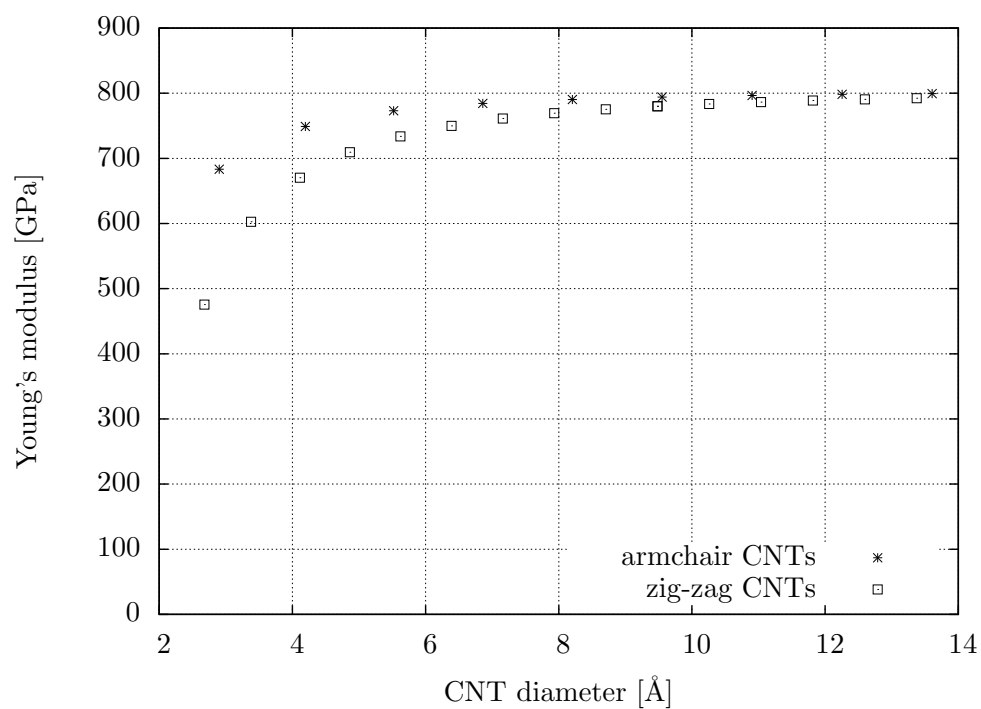


Figure 4. Young's modulus for armchair and zig-zag CNTs

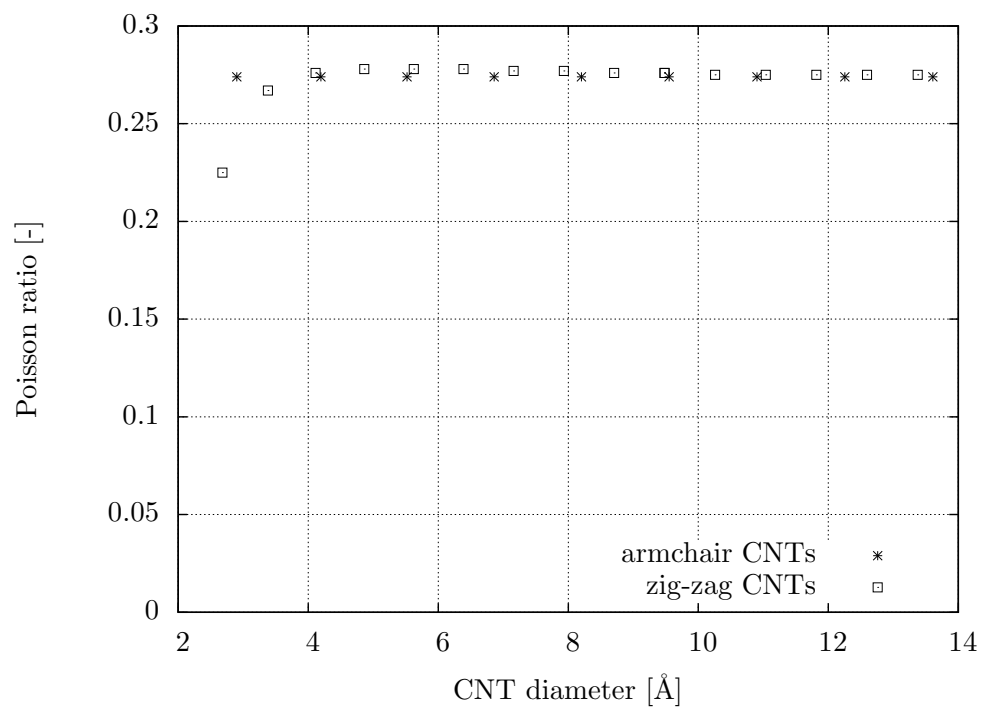


Figure 5. Poisson ratio for armchair and zig-zag CNTs

5. MECHANICAL BEHAVIOR OF MWNTS AND SELECTED CNT ASSEMBLIES

5.1 Modeling

The preceding sections dealt with the elastic behavior of individual CNTs. In contrast to this, the present section discusses the behavior of groups of several CNTs arranged in a specific pattern. In the present work this includes in particular the investigation of double wall carbon nanotubes (DWNTs) which are MWNTs with only two shells. The focus of the investigation of these types of structures lies in the interaction behavior of the individual nanotubes within the nanotube assembly. The CNTs can interact with each other via van-der-Waals bonds. These van-der-Waals bonds and the resulting van-der-Waals forces can be observed between each carbon atom pair in the structure. This results in a huge number of van-der-Waals bonds. During the following investigations these van-der-Waals bonds have to be considered with the help of an appropriate potential. One suitable choice is the Lennard-Jones potential

$$U_{ij}^{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (6)$$

It describes the van-der-Waals bond between the two atoms i and j . Here, ϵ and σ are the so called Lennard-Jones parameters which are chosen in dependence of the chemical element and type of the bonded atoms. Since the present work deals with carbon nanotubes, the parameters for a bond between two sp^2 -hybridized carbon atoms have to be chosen. Furthermore, r depicts the distance between the two atoms. The overall behavior of the CNT assembly can be characterized by the total potential. This includes the contribution of all the relevant van-der-Waals bonds in the system. As a result of the fast decreasing Lennard-Jones potential it is not necessary to include all the van-der-Waals bonds, but only the ones contributing by a significant quantity to the total potential. The selection whether a bond has to be taken into account or not is commonly done by the interatomic distance r . If the distance exceeds a certain value, the bond can be neglected without a significant loss of accuracy. In order to avoid double considerations of van-der-Waals bonds the following scheme to calculate the total potential is chosen

$$U^{total} = \sum_{\alpha=1}^{s-1} \sum_{\delta=\alpha+1}^s \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\delta} U_{ij}^{LJ}. \quad (7)$$

Here, s is the number of incorporated CNTs in the investigated CNT assembly, while N_α and N_δ are the corresponding numbers of atoms in CNT $\alpha \in (1, \dots, s-1)$ and $\delta \in (\alpha+1, \dots, s)$. For the example of a displacement controlled DWNT pull-out test, as given in section 5.2, the number of CNTs is $s = 2$. Hence equation (7) is reduced to

$$U^{total} = \sum_{\alpha=1}^1 \sum_{\delta=2}^2 \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\delta} U_{ij}^{LJ} = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} U_{ij}^{LJ}. \quad (8)$$

It has to be noted, that in the investigation of CNT assemblies, the individual CNTs are considered to be rigid structures. The permissibility of this assumption can be explained by the fact, that the forces due to the van-der-Waals bonds are small compared to the bonding forces within the CNTs. One can also put it that way, that the covalent bonds assuring the cohesion of the individual CNT structure are much stronger than the van-der-Waals bonds in between the CNTs.

The total potential can be depicted as n -dimensional surface, where n is the number of degrees of freedom. This potential surface describes the mechanical behavior of the CNT assembly and can be investigated e.g. in terms of finding equilibrium positions of the CNT assembly. This results in a multivariate minimization (n -dimensional) of the potential surface since the equilibrium positions distinguish themselves as maxima or minima in the potential surface. Maxima would mark unstable and minima would mark stable equilibrium positions. Also the consideration of external forces or moments is possible. The forces between specific partners in the CNT assembly can be determined by the calculation of the corresponding derivatives of the overall potential. Since the potential is highly nonlinear with respect to their degrees of freedom, a suitable method for minimizing the potential surface needs to be chosen. This was done by applying a nonlinear conjugate gradient method using a Polak-Ribière formula.

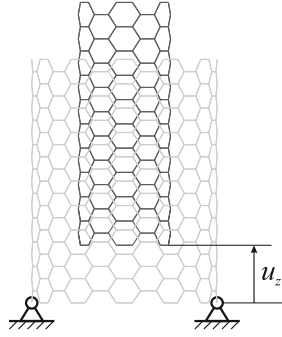


Figure 6. Schematic representation of the displacement controlled pull-out test consisting of two CNTs forming a DWNT

5.2 Numerical simulation and results of a DWNT pull-out test

A simple and intuitively understandable example for an application of the model given above is the investigation of a DWNT pull-out test. The test is outlined as follows: The inner tube starts at a position outside of the outer tube and is then moved path-controlled all the way through the outer tube up to a position where the inner tube is located again completely outside of the outer tube. Since in this virtual experiment all the degrees of freedom with exception of the displacement u_z are fixed, see figure 6, this pull-out test is an example for an one dimensional problem. During the test, several important parameters are plotted, see figures 7 and 8. This includes the smallest interatomic distance r_{min} , which is the smallest beeline between two atoms occurring in the structure. In this plot, the zero crossing of the Lennard-Jones potential (see also figure 7 top right) is introduced as horizontal line r_0 . Furthermore, the plot of the Lennard-Jones potential for a single van-der-Waals bond is given in figure 7 (top right) and figure 8 (top right). In order to facilitate the explanation of the DWNT behavior, two specific values of the interatomic distance r are marked in the plot:

- the smallest interatomic distance when the two nanotubes are perfectly aligned ($u_z = 0$): $r_{min}^{u_z=0}$
- the zero crossing of the Lennard-Jones potential r_0 .

The figures 7 and 8 give the results for two different DWNTs consisting of (6,6)/(10,10) as well as (6,6)/(11,11) armchair tube combinations all with a length of 10 unit cells. Additionally, also the total potential U^{total} and the force F the inner (and outer) tube are subjected to during the pull-out are recorded.

One interesting result of the test is, that for the (6,6)/(10,10) DWNT no stable equilibrium positions for the inner tube inside the outer tube can be found, while the (6,6)/(11,11) DWNT shows such a stable equilibrium position when both tubes are aligned ($u_z = 0$). The other graphs given in the figures 7 and 8 allow the explanation of this phenomenon. Figure 7 (top left) shows, that for the (6,6)/(10,10) DWNT the smallest interatomic distance $r_{min}^{u_z=0}$ is smaller than r_0 . In figure 7 (top right), this $r_{min}^{u_z=0}$ is also given. It can be easily observed, that the bond(s) with the length $r_{min}^{u_z=0}$, or close to it, have a huge impact on the total potential U^{total} due to the high values for the Lennard-Jones potential especially for short bonds. This is also reflected in figure 7 (bottom left) in which the total potential U^{total} is larger than zero.

In contrast, for the (6,6)/(11,11) DWNT the smallest interatomic distance has almost crossed the r_0 line of the Lennard-Jones potential. The much smaller contributions of the van-der-Waals bonds with the smallest length $r_{min}^{u_z=0}$, see figure 8 (top right), result in the switching of the instable equilibrium position into a stable equilibrium position.

Furthermore, also conclusions regarding the nanotube forces can be made. The nanotube force plots in figures 7 (bottom right) and 8 (bottom right) depict the force F the inner tube is subjected to during the path-controlled pull-out. When the force plot of the (6,6)/(10,10) DWNT is compared to the one of the (6,6)/(11,11) DWNT, one can recognize the change of the algebraic sign of the nanotube force. This means, that for the first mentioned (6,6)/(10,10) DWNT, the outer tube works “against” the insertion of the inner tube, while for the (6,6)/(11,11) DWNT, the outer tube wants to pull the inner tube inside.

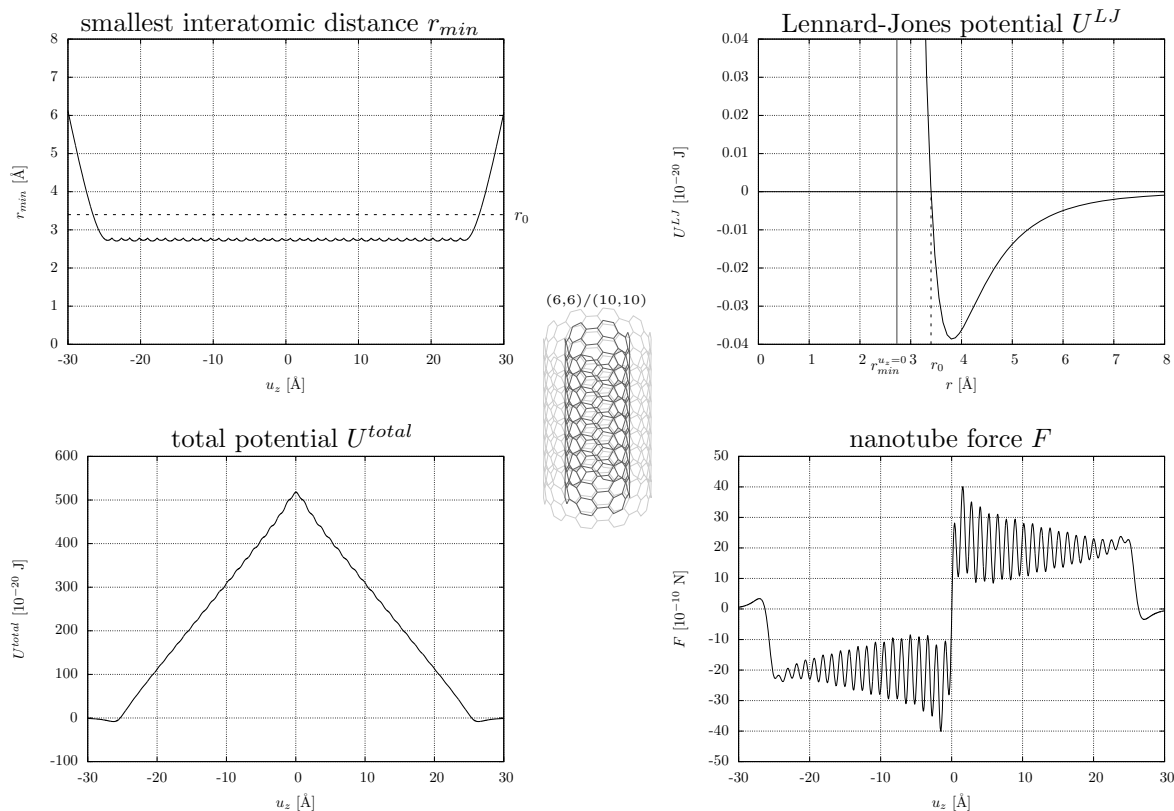


Figure 7. Results for the pull-out test with a (6,6)/(10,10) DWNT with a length of ten unit cells

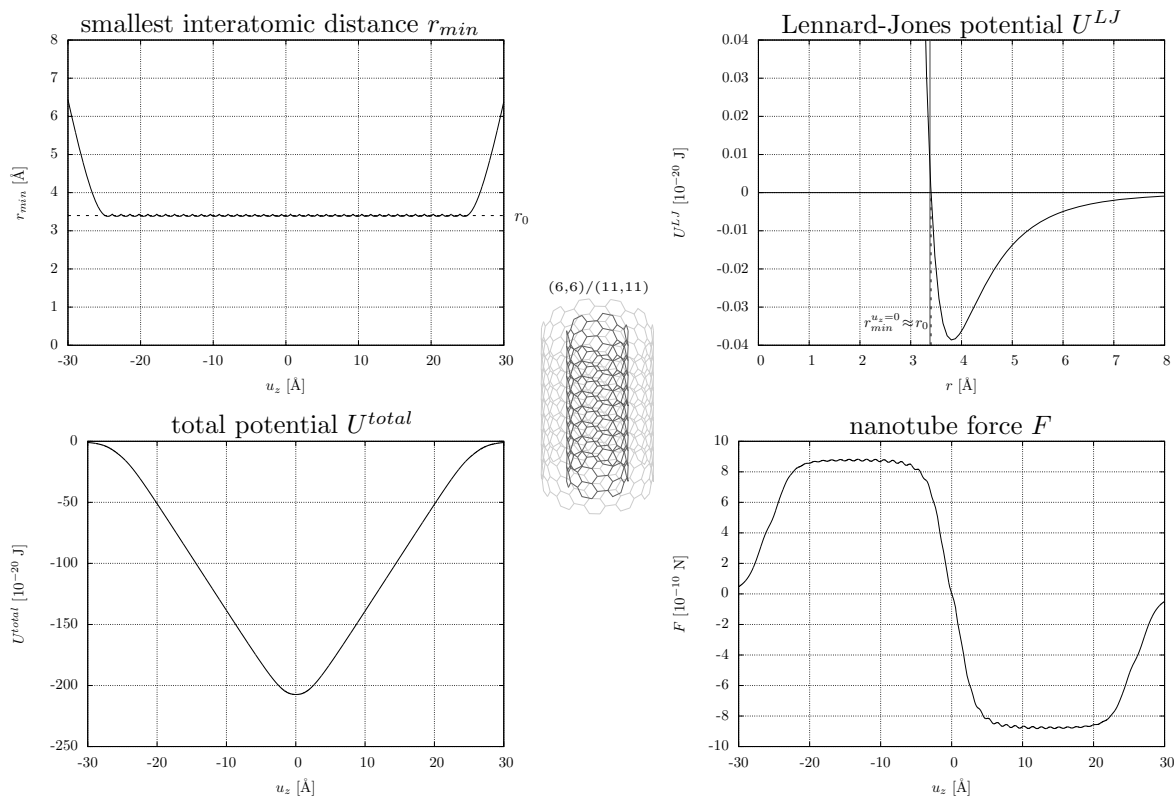


Figure 8. Results for the pull-out test with a (6,6)/(11,11) DWNT with a length of ten unit cells

6. CONCLUSION AND OUTLOOK

This work presents methods applicable for the calculation of the mechanical behavior of individual SWNTs as well as of CNT assemblies.

Regarding the investigation of individual SWNTs a model based on a molecular structural mechanics approach was briefly introduced. It uses beam elements to represent the covalent bonds in the CNT. The mandatory geometrical parameters of the beam as well as the material parameters were calculated with the help of a chemical force field description. The parameters were obtained by a correlation of the deformations in chemical bonds with the corresponding deformations in the mechanical beam representation. The model was then used to set up a virtual tensile test in order to obtain the Young's modulus and the Poisson ratio of armchair and zig-zag CNTs. The results show a remarkably high Young's modulus of around 0.8 TPa and a Poisson ratio of approximately 0.275.

For studying CNT assemblies, a method based on the calculation and examination of a total potential surface was proposed. Here, all the relevant contributions of van-der-Waals bonds represented by the Lennard-Jones potential are considered and summed up in order to obtain the total potential surface. The potential surface can be examined for instance by numerical multivariate minimization, for example by using a nonlinear conjugate gradient method. In order to demonstrate the method, a path-controlled pull-out test of a double wall carbon nanotube (DWNT) was investigated. The formation of a stable equilibrium position of the inner CNT inside the outer CNT was shown. The explanation of this phenomenon was given by analyzing the contributions of the shortest van-der-Waals bonds.

Future applications of the methods presented in this paper aim on the detailed investigation of the behavior of fibers spun from CNTs. In order to do this, representative CNT assemblies will be investigated in order to obtain a general understanding of mechanical behavior, strength and stiffness of the fiber.

ACKNOWLEDGMENTS

The support of the German Science Foundation (DFG) within the grant WA2323/4-1 is gratefully acknowledged.

REFERENCES

- [1] Iijima, S., "Helical microtubules of graphitic carbon," *Nature* **354**, 56 (1991).
- [2] Radushkevich, L. and Lukyanovich, V., "About the structure of carbon formed by thermal decomposition of carbon monoxide on iron substrate," *J. Phys. Chem. (Moscow)* **26**, 88–95 (1952).
- [3] Chou, T.-W., Gao, L., Thostenson, E. T., Zhang, Z., and Byun, J.-H., "An assessment of the science and technology of carbon nanotube-based fibers and composites," *Composites Science and Technology* **70**(1), 1–19 (2010).
- [4] De Volder, M. F., Tawfick, S. H., Baughman, R. H., and Hart, A. J., "Carbon nanotubes: present and future commercial applications," *Science* **339**(6119), 535–539 (2013).
- [5] Baughman, R. H., Cui, C., Zakhidov, A. A., Iqbal, Z., Barisci, J. N., Spinks, G. M., Wallace, G. G., Mazzoldi, A., Rossi, D. D., Rinzler, A. G., Jaschinski, O., Roth, S., and Kertesz, M., "Carbon nanotube actuators," *Science* **284**, 1340–1344 (1999).
- [6] Lu, W., Zu, M., Byun, J.-H., Kim, B.-S., and Chou, T.-W., "State of the art of carbon nanotube fibers: opportunities and challenges," *Advanced Materials* **24**(14), 1805–1833 (2012).
- [7] Foroughi, J., Spinks, G. M., Wallace, G. G., Oh, J., Kozlov, M. E., Fang, S., Mirfakhrai, T., Madden, J. D., Shin, M. K., Kim, S. J., et al., "Torsional carbon nanotube artificial muscles," *Science* **334**(6055), 494–497 (2011).
- [8] Kosidlo, U., Omastová, M., Micusík, M., Ćirić-Marjanović, G., Randriamahazaka, H., Wallmersperger, T., Aabloo, A., Kolaric, I., and Bauernhansl, T., "Nanocarbon based ionic actuators - a review," *Smart Materials and Structures* **22**(10), 104022 (2013).
- [9] Schnorr, J. M. and Swager, T. M., "Emerging applications of carbon nanotubes," *Chemistry of Materials* **23**(3), 646–657 (2011).
- [10] Sánchez-Portal, D., Artacho, E., Soler, J. M., Rubio, A., and Ordejón, P., "Ab initio structural, elastic, and vibrational properties of carbon nanotubes," *Phys. Rev. B* **59**(19), 12678–12688 (1999).

- [11] Domínguez-Rodríguez, G., Tapia, A., and Avilés, F., “An assessment of finite element analysis to predict the elastic modulus and Poissons ratio of singlewall carbon nanotubes,” *Computational Materials Science* **82**, 257–263 (2014).
- [12] Hernández, E., Goze, C., Bernier, P., and Rubio, A., “Elastic properties of C and $B_xC_yN_z$ composite nanotubes,” *Phys. Rev. Lett.* **80**(20), 4502–4505 (1998).
- [13] Odegard, G. M., Gates, T. S., Nicholson, L. M., and Wise, K. E., “Equivalent-continuum modeling of nano-structured materials,” *Composites Science and Technology* **62**, 1869–1880 (2002).
- [14] Chang, T., “A molecular based anisotropic shell model for single-walled carbon nanotubes,” *Journal of the Mechanics and Physics of Solids* **58**(9), 1422–1433 (2010).
- [15] Li, C. and Chou, T.-W., “A structural mechanics approach for the analysis of carbon nanotubes,” *International Journal of Solids and Structures* **40**, 2487–2499 (2003).
- [16] Tserpes, K. and Papanikos, P., “Finite element modeling of single-walled carbon nanotubes,” *Composites: Part B* **36**, 468–477 (2005).
- [17] Eberhardt, O. and Wallmersperger, T., “Mechanical properties and deformation behavior of carbon nanotubes calculated by a molecular mechanics approach,” *Smart Structures and Systems* **13**(4), 685–709 (2014).
- [18] Chen, W.-H., Cheng, H.-C., and Liu, Y.-L., “Radial mechanical properties of single-walled carbon nanotubes using modified molecular structure mechanics,” *Computational Materials Science* **47**, 985–993 (2010).
- [19] Meo, M. and Rossi, M., “Prediction of Young’s modulus of single wall carbon nanotubes by molecular-mechanics based finite element modelling,” *Composites Science and Technology* **66**, 1597–1605 (2006).
- [20] Giannopoulos, G., Kakavas, P., and Anifantis, N., “Evaluation of the effective mechanical properties of single walled carbon nanotubes using a spring based finite element approach,” *Computational Materials Science* **41**(4), 561–569 (2008).
- [21] Zhao, J., Jiang, J.-W., Jia, Y., Guo, W., and Rabczuk, T., “A theoretical analysis of cohesive energy between carbon nanotubes, graphene and substrates,” *Carbon* **57**, 108–119 (2013).
- [22] Dresselhaus, M. S., Dresselhaus, G., and Saito, R., “Physics of carbon nanotubes,” *Carbon* **33**, 883–891 (1995).
- [23] Cox, B. J. and Hill, J. M., “Exact and approximate geometric parameters for carbon nanotubes incorporating curvature,” *Carbon* **45**(7), 1453 – 1462 (2007).